

Almost Exact Exchange At Almost No Cost

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A recently developed semiclassical approximation to exchange in one dimension is shown to be almost exact, with essentially no computational cost. The variational stability of this approximation is tested, and its far greater accuracy relative to local density functional calculations demonstrated. Even a fully orbital-free potential-functional calculation (no orbitals of any kind) yields little error relative to exact exchange, for more than one orbital.

Electronic structure problems in chemistry, physics, and materials science are often solved via the Kohn-Sham method of density functional theory (DFT)[1, 2], which balances accuracy with computational cost. For any practical calculation, the exchange-correlation (XC) energy must be approximated as a functional of the density. The basic theorems of DFT guarantee its uniqueness, but give no hint about constructing approximations. The early local density approximation (LDA)[2], much used in solid state physics, was the starting point for today's more accurate methods such as the generalized gradient[3, 4] and hybrid[5] approximations. But a systematic approach for deriving these has not yet been found, a fact that is reflected by the plethora of XC approximations that are continuously created[6].

This lack also inspires many approaches beyond traditional DFT, such as orbital-dependent functionals like exact exchange (EXX) [7, 8], use of the random phase approximation[9], and (first-order) density matrix functional theory[10]. While any of these can produce higher accuracy, their computational cost is typically much greater, and none have yet yielded a universal improvement over existing Kohn-Sham (KS) DFT. Perhaps the most ubiquitous DFT method is that of hybrid functionals, which replace some generalized gradient exchange with exact exchange. Hybrids are now standard in molecular calculations, and yield more accurate thermochemistry in most cases[6]. Furthermore, range-separated hybrids [11], where the exchange is treated in a Hartree-Fock fashion, typically yield much improved band gaps for many bulk solids[12]. However, their computational cost in plane-wave codes can be up to a thousand times higher than that of generalized gradient approximation calculations, making such methods much less useful in practice[13]. Implicit within quantum mechanics is that exact or approximate solutions of the Schrodinger equation are functionals of the *potential*, but the methodology of DFT is built around the density instead. Pioneering work[14] derived the duality of density and potential functionals in the context of an orbital-dependent KS-DFT calculation. More recently, the formalism of a pure potential functional the-

ory (PFT) has been developed[15–17], and approximations for non-interacting fermions in simple model systems have been tested[18, 19]. The leading corrections to Thomas-Fermi theory are explicit functionals of the potential[18, 20, 21], and inclusion of these corrections yields approximations that are typically much more accurate than their DFT counterparts.

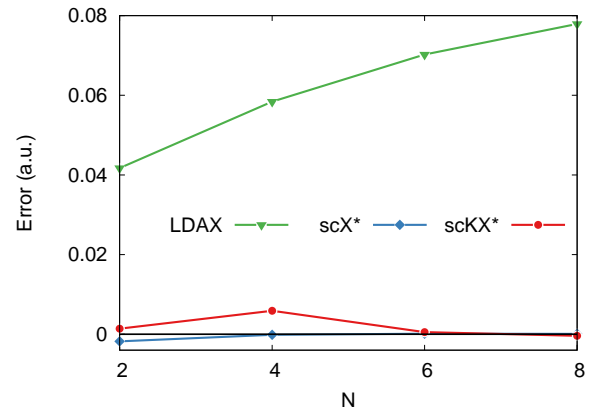


FIG. 1. Error in the total energy made by LDA exchange (LDAX), semiclassical exchange (scX), and semiclassical kinetic and exchange (scKX) for N spin-unpolarized, interacting fermions in a well (see Tab. I).

Here we go beyond the non-interacting case by including both Hartree and exchange components of the electron-electron interaction to illustrate the promise of PFT for avoiding the cost of orbital-dependent DFT calculations. In Fig. 1, we show the errors made in the total energy of one-dimensional electrons in a potential with box boundaries, using a recently developed semiclassical PFT approximation[22]. scX is a simple explicit formula for the exchange energy in terms of the KS potential, and here is evaluated on the self-consistent potential in a LDA exchange (LDAX) calculation. Even for only one occupied orbital, the error is less than 5% of LDAX, and is negligible for two or more orbitals, even though the exchange energy grows. If such a formula existed for three dimensions, the cost of (almost) EXX would be vanishingly small. We also (i) develop the KS equation of PFT

for interacting particles without recourse to DFT quantities, (ii) give an algorithm for solving this equation, (iii) implement that algorithm in 1d, and (iv) perform purely PFT calculations.

To begin, the ground-state energy of N electrons in an external potential $v(\mathbf{r})$ is given by

$$E_0 = \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V} | \Psi \rangle, \quad (1)$$

where the search is over all normalized, antisymmetric Ψ , and \hat{T} is the kinetic energy operator, \hat{V}_{ee} the electron-electron repulsion, and $\hat{V} = \sum_i v(\mathbf{r}_i)$ the one-body operator. We use Hartree atomic units ($e^2 = \hbar = m_e = 1$) and suppress spin indices for simplicity. The universal potential functional[17] is

$$F[v] = \langle \Psi_0[v] | \hat{T} + \hat{V}_{ee} | \Psi_0[v] \rangle \quad (2)$$

where $\Psi_0[v]$ is the ground-state wavefunction of $v(\mathbf{r})$, so

$$E_0 = \min_{\tilde{v}} \left(F[\tilde{v}] + \int d\mathbf{r} n[\tilde{v}](\mathbf{r}) v(\mathbf{r}) \right) \quad (3)$$

where $n[v](\mathbf{r})$ is the ground-state density of $v(\mathbf{r})$. In the exact case, $\tilde{v}(\mathbf{r}) = v(\mathbf{r})$, but this is not necessarily true for approximations.

In previous work[17], it was shown that in PFT, once $n[v](\mathbf{r})$ is given, $F[v]$ can be deduced, either by a coupling-constant integral or a virial relation. When applied to non-interacting fermions, an approximation $n_s[v_s](\mathbf{r})$ yields an approximation $T_s[v_s]$, where $v_s(\mathbf{r})$ is the potential in this non-interacting case. Now we introduce a direct approximation to the XC energy, $E_{xc}[v_s]$, as a functional of the KS potential, and ask: How can these two approximations be used to find the ground-state energy of interacting fermions? This question differs from that of deducing the KS equations in DFT, because here the approximation is a potential functional, not a density (or orbital-dependent) functional.

To deduce the answer, we write the potential functional as a functional of $v_s(\mathbf{r})$ rather than $v(\mathbf{r})$ [16]:

$$\bar{F}[v_s] = F[v[v_s]] = T_s[v_s] + U[v_s] + E_{xc}[v_s], \quad (4)$$

i.e., all are functionals of the KS potential (which is uniquely determined by $v(\mathbf{r})$), where U is the Hartree energy and E_{xc} is everything else. As mentioned above, with a given $n_s[v_s](\mathbf{r})$, we can determine T_s and U . Applying Eq. (3), but now searching over trial KS potentials, yields, via the Hohenberg-Kohn theorem[14]

$$E_0 = \min_{v_s} \left(\bar{F}[v_s] + \int d\mathbf{r} n_s[v_s](\mathbf{r}) v(\mathbf{r}) \right) \quad (5)$$

where we call the minimizing KS potential $\tilde{v}_s(\mathbf{r})$. To find $\tilde{v}_s(\mathbf{r})$, we use the Euler equation[16]:

$$\left. \frac{\delta E_{v_0}[v_s]}{\delta v_s(\mathbf{r})} \right|_{\tilde{v}_s} = 0 \quad (6)$$

for both the interacting and non-interacting systems, and equate potentials:

$$v'_s[\tilde{v}_s](\mathbf{r}) = v_0(\mathbf{r}) + \int d\mathbf{r}' \chi_s^{-1}[\tilde{v}_s](\mathbf{r}', \mathbf{r}) \left. \frac{\delta E_{\text{HXC}}[v_s]}{\delta v_s(\mathbf{r}')} \right|_{\tilde{v}_s}, \quad (7)$$

where $E_{\text{HXC}} = U + E_{\text{XC}}$, $\chi_s[\tilde{v}_s](\mathbf{r}', \mathbf{r}) = \delta n_s[v_s](\mathbf{r}') / \delta v_s(\mathbf{r})|_{\tilde{v}_s}$ is the one-body density-density response function and:

$$v'_s[\tilde{v}_s](\mathbf{r}) = - \int \chi_s^{-1}[\tilde{v}_s] \left. \frac{\delta T_s[v_s]}{\delta v_s} \right|_{\tilde{v}_s}. \quad (8)$$

as shown in Ref. 16. Note that $v'_s = \tilde{v}_s$ only if $T_s[v_s]$ and $n[v_s]$ together satisfy the noninteracting Euler equation, such as for the exact functionals, as in Ref. [14]. The solution of Eq. (7) yields the minimizing KS potential $\tilde{v}_s(\mathbf{r})$, once $n_s[v_s](\mathbf{r})$ and $E_{\text{HXC}}[v_s]$ are given. But since Eq. (7) requires computing the inverse of χ_s , which becomes costly with increasing particle number, we instead directly minimize Eq. (5).

We next turn to actual calculations, using approximate potential functionals. Applying similar integration techniques in the complex energy plane as in Refs. 15 and 18, we obtain a semiclassical potential functional approximation (PFA) to the one-body reduced density matrix

$$\gamma_s^{sc}(x, x') = \sum_{\lambda=+,-} \frac{\lambda \sin[\theta_F^\lambda(x, x')] \text{cosec}[\alpha_F^\lambda(x, x')/2]}{2T_F \sqrt{k_F(x)k_F(x')}}, \quad (9)$$

of N fermions in a one-dimensional potential, inside a box, whose chemical potential is above the potential everywhere. Here $\theta^\pm(x, x') = \theta(x) \pm \theta(x')$, $\alpha^\pm(x, x') = \alpha(x) \pm \alpha(x')$, $\theta(x) = \int_0^x dx' k(x')$ denotes the semiclassical phase, $k(x) = \sqrt{2(\mathcal{E} - v(x))}$ the wave vector, \mathcal{E} is the energy, $\alpha(x) = \pi\tau(x)/T$, $\tau(x) = \int_0^x dx' k^{-1}(x')$ the traveling time of a classical particle in the potential $v(x)$ from one boundary to the point x at a given energy, and $T = \tau(L)$ [15]. A subscript F denotes evaluation at the Fermi energy, which is found by requiring the wavefunctions to vanish at the edge, i.e., $\Theta_F(L) = (N + 1/2)\pi$. The derivation and implications for DFT of this expression is given elsewhere[22]. As $x \rightarrow x'$, the diagonal reduces to the known semiclassical approximation for the density[15] and two derivatives yield the corresponding approximation to the non-interacting kinetic energy[17]. For a given electron-electron repulsion, $v_{ee}(u)$, where $u = |x - x'|$ denotes the separation between electrons, the semiclassical exchange is:

$$E_x^{sc}[v_s] = -\frac{1}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx dx' |\gamma_s^{sc}[v_s](x, x')|^2 v_{ee}(u). \quad (10)$$

We next test both the accuracy and the stability of the semiclassical approximations relative to standard DFT. In all cases, we put the ‘electrons’ in pairs in a 1d

box of unit length, with a one-body potential $v(x) = -5\sin^2(\pi x)$, and repelling each other via $\exp(-\alpha u)$ with $\alpha = 4$. These parameters are chosen so that even for $N = 2$, the condition on the Fermi energy is satisfied.

We first define what *exact* calculation we shall use to analyze our results. In this context, it is a full OEP calculation using the exact orbital expression for exchange. Such a calculation produces the exact KS kinetic and exchange energies and KS potential on the self-consistent EXX density for the problem. Next, we define LDAX and check its performance. The LDAX energy per electron is

$$\epsilon_x^{\text{LDA}}(n(x)) = -\frac{\arctan \beta}{\pi} + \frac{\ln(1 + \beta^2)}{2\pi\beta} \quad (11)$$

with $\beta = 2\pi n(x)/\alpha$. In Tab. I we report exact total energies and errors of several approximate calculations, as a function of (double) occupation of orbitals. We see that LDAX makes a substantial error for $N = 2$ which grows with N , although E_x itself grows, so the fractional error is vanishing (as it must[15]) as $N \rightarrow \infty$. A modern generalized gradient approximation might reduce this error by a factor of 2 or 3. In Tab. II, we list the total energy and its various components for four particles in the well. Since the energy error is almost entirely given by the exchange error, this means the LDAX density and component energies are very accurate, and the corresponding LDAX KS potential quite accurate. Due to the variational principle, the small differences in the different energy components almost cancel.

Our first new calculation is a post-LDA calculation of the exchange energy using the semiclassical approximation of Eq. 10, i.e., $E_x^{\text{sc}}[v_s^{\text{LDAX}}]$. This is orbital-free exchange but using the potential rather than the density as the basic variable. The error is plotted in Fig. 1, and tabulated next to the LDAX results in Tabs. I and II, denoted scX*, where the * indicates a non-variational calculation. Even for $N = 2$, the error is an order of magnitude smaller than LDAX. As N grows, the error shrinks very rapidly, even in absolute terms, because the semiclassical corrections to LDAX capture the leading corrections in powers of $1/N$ [18, 19]. In the next column over, we even use the semiclassical kinetic energy as well (scKX) on the LDAX KS potential, and see that, although the errors can be much larger, they are still far below those of LDAX. These results show that the semiclassical exchange and even kinetic energy can be extracted from a simple LDAX self-consistent calculation, yielding much smaller errors than LDAX. Thus results almost identical to expensive EXX OEP calculations can be found at essentially no cost with a PFA exchange that includes the leading asymptotic corrections to LDAX.

But such a recipe, while showing the accuracy of resulting exchange energies quickly, can be criticized for not being variational, i.e., not the result of any self-consistent minimization. Our second type of calculation is to again use the semiclassical PFT exchange within

TABLE I. Total EXX energy and respective errors of self-consistent as well as perturbative post-LDAX(*) calculations within LDAX, scX, and scKX for N spin-unpolarized fermions interacting via $\exp(-4u)$ in an external potential $v(x) = -5\sin^2(\pi x)$ within a box of unit length.

N	E^{EXX}	E_x^{EXX}	error $\cdot 10^3$				
			LDAX	scX*	scKX*	scX	scKX
2	2.81	-0.52	41.72	-1.79	1.40	-3.10	-29.60
4	39.04	-1.26	58.41	-0.15	5.89	-3.86	-1.14
6	126.10	-2.10	70.24	0.14	0.53	-1.20	0.47
8	283.70	-2.98	77.91	0.08	-0.40	-0.10	-1.76

TABLE II. Energy components of self-consistent calculations within LDAX, semiclassical exchange (scX), and a semiclassical approximation of all energy components (scKX) for 4 'electrons' in the same problem as in Tab. I.

	EXX	error $\cdot 10^3$		
		LDAX	scX	scKX
E	39.04	58.41	-3.86	-1.14
T_s	49.44	1.22	0.34	1.22
V_{ext}	-12.72	-1.38	0.07	4.56
U	3.58	0.003	0.02	-5.90
E_x	-1.26	58.56	-4.29	-1.02

a regular KS-DFT calculation. The resulting expression for the total energy is then minimized. We expand the KS potential in Chebyshev polynomials and use the Nelder-Mead method[23, 24] to optimize the expansion coefficients. A similar technique was used for the EXX case[25, 26], where the exchange energy was the usual Fock integral. We should point out treating this method variationally required additional constraints than the perturbative case. For certain systems the minimization would find pathological potentials that behave badly near the box boundaries but nevertheless minimize the total energy. Conveniently the semiclassical approximations developed contain an error check in the form of the normalization of the semiclassical density. If this normalization deviated by 1% or more from N , we add a large penalty to the total energy. This is then used to exclude such potentials that lie far from the domain of applicability of our approximations and leads to the good results of Tab. I.

In Tabs. I and II, next to the scKX* columns, we list the scX results of this procedure. The error remains much smaller than that of LDAX, and rapidly reduces with increasing N . This is consistent with our previous semiclassical approximations for the density and kinetic energy[15, 17–19]. However, errors are also typically much larger than those of the non-self-consistent calculation (scX*), showing that the variational properties are less robust than in LDAX. This is not surprising, given that LDAX satisfies a crucial symmetry condition that scX does not[17, 19]. This is related to the very incorrect

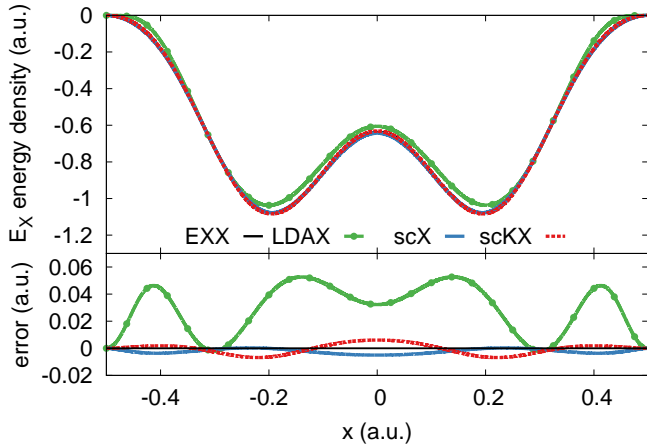


FIG. 2. Exchange energy density of 4 spin-unpolarized fermions for the same problem as in Tab. I. The upper plot shows the EXX energy as well as result from a self-consistent calculation via LDAX, scX, and scKX. The respective errors are plotted in the lower panel.

local minima that the procedure finds if not restrained, as mentioned above.

To illustrate better the improvement in going from LDAX to scX, we plot the exchange energy densities in Fig. 2, and their errors. The scX density greatly improves over the LDAX density everywhere in space (except where LDAX accidentally matches the exact value). This is in stark contrast to the well-known difficulty of defining and comparing energy densities in generalized gradient approximations and other DFT approximations[27].

Finally, our *piece de resistance* is to run a pure PFT calculation, using semiclassical expressions for all energy components, not just the exchange energy, by directly minimizing Eq. (5). This is a true orbital-free calculation, the PFT analog of orbital-free DFT, and we compare its results to a full OEP EXX calculation. We denote this scKX, and its results are in the far right columns of Tabs. I and II.

First, note that because we have now approximated the kinetic energy, we would be doing extremely well to even match an LDAX calculation. However, we see that in every case, the errors are *smaller* than LDAX. This is the basic criterion for a successful orbital-free functional: its errors are smaller than typical errors in XC approximations. However, we also note that for any $N > 2$, its errors are so small (below 2 mH) that they match those of exact exchange for most practical purposes. Finally, note that inaccuracies for $N = 1$ or 2 do not matter, since the exchange energy for those cases is known exactly via the Hartree energy.

Looking more closely, it is remarkable that scKX is more accurate than scX for $N = 2$ and 4. If we look at the individual energy components in Tab. II, we see that, e.g., the Hartree energy is far more accurate in scX than

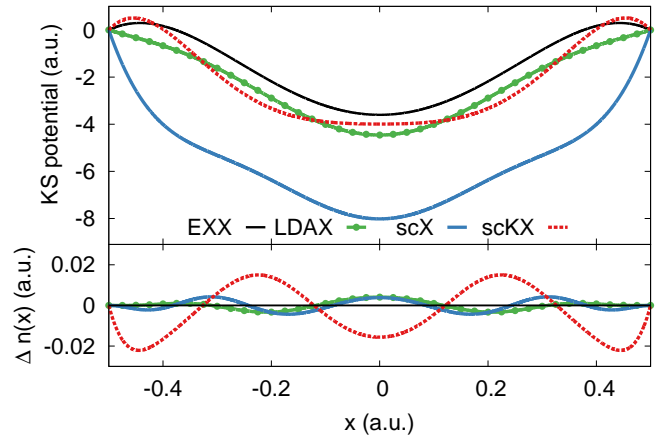


FIG. 3. Upper plot: Converged KS potentials of EXX, LDAX, scX, and scKX runs for the same problem as in Tab. I with 4 spin-unpolarized fermions. Lower plot: Error in the respective, converged densities with respect to EXX.

scKX, while the reverse is true for E_x . This implies that the density is quite inaccurate in scKX, but substantial cancellation of errors occurs. To see this, in Fig. 3 we plot both the KS potentials and density errors for the different calculations, showing the much greater errors in scKX. However, the cancellation of errors might well be due to the balanced nature of the calculation, since *all* energy components have been derived from a single approximation for the density matrix[16]. Only extensive testing for many different circumstances can determine if this is a general phenomenon and if so, where it fails.

Thus minimizing our PFA reproduces the result of a self-consistent EXX KS calculation. Furthermore, as the number of electrons increases, not only does the PFA computational effort not increase significantly, but the accuracy also increases. The Fock integral required in EXX or hybrid calculations scales formally as $\Omega^2 N^2$ where Ω is the number of real space grid points used in our 1d box. Our semiclassical expression simply scales as Ω^2 . As N increases, Ω should scale linearly in order to preserve the ratio of grid points to orbital nodes. Thus the Fock integral scales as N^4 while our approximation scales much more favourably as N^2 . In quantum chemistry, evaluation of the Fock energy has been the focus of much effort to improve the scaling, but at best the scaling can be reduced to roughly N^3 (e.g., when localized basis sets and various optimization techniques are used). Thus our scaling remains advantageous. The scKX calculation is completely orbital-free and so avoids solving the KS equation. Either due to direct diagonalization or the orthogonalization of orbitals depending on the method used, the KS scheme scales as N^3 , while scKX scales as N^2 due to exchange (the other energy components scale as N). Thus the PFT method can ef-

fectively reproduce the result of an EXX KS calculation while requiring a fraction of the computational cost. Substituting EXX with our semiclassical exchange may also be done in the hybrid functional approach to DFT (although treated within the OEP framework), where the fraction of EXX mixed in with a standard DFT functional may be replaced. Calculating this EXX energy is often the costliest part for hybrid calculations. By using the semiclassical PFA exchange one could vastly speed up such calculations without a significant loss in accuracy.

In conclusion we have shown that an approximation to the exchange energy is *almost* exact and does not require any orbital information in the framework of PFT. In both accuracy and efficiency, the PFT method performs better than high-level KS-DFT calculations. If ongoing work to extend the method to 3d systems is successful, electronic structure calculations could be sped up by several orders of magnitudes, allowing large systems that are currently out of reach with density functional methods to be studied.

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